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Removal of m-chlorophenol from Wastewater by Adsorption onto Flyash Produced from Thermal power plant: Kinetic Modeling Studies

B. K. Singh[1]*, Pragya Nema[2], Nandini Tembhre[3], Anil Kushwaha[4]

[1,2,3,4] Deptt. of chemistry, Govt. M. H College of H. Sc. & Science, Autonomous, and Jabalpur (M. P) 482001, India

ABSTRACT

Adsorption technique is widely used for removal of toxic organics from aqueous solutions. As commercial activated carbon is an efficient adsorbent, it's widespread used is restricted due to its high cost and substantial lost during regeneration. The aim of this study is to investigate the possibility of flyash (FA) as an alternative adsorbent for phenols removal from aqueous solution .The removal characteristics of m-chlorophenol (MCP) from aqueous solution by flyash is investigated under various conditions of contact time, particle size, pH, concentration and temperature. The level of uptake of m-chlorophenol by flyash decreased with increasing particle size and pH but increases with temperature. Rate constants for different conditions are evaluated using first-order kinetics. The experimental results underlined the potential of flyash for removal of m-chlorophenol from wastewater. The main mechanisms involved in the removal of m-chlorophenol from solution by flyash are electron –withdrawing effect of chloro group of benzene ring and adsorption at the surface of the flyash. It is found that these low cost flyash adsorbent demonstrated good removal capability of phenols and hence can be used economically on large scale for m-chlorophenol.

Key Words: Flyash, m -chlorophenol, adsorption, kinetics, mechanism.

INTRODUCTION

Wastewater congaing phenolic compounds are a serious environmental problem releasing into the environment without treatment. The toxic and hazardous nature of phenol and its derivatives have been well documented and can cause several health problems.[1] it is of major concern that organic pollutants are present in the environment because of their toxicity, bio-accumulative tendency, and threat to human life and the environment. Phenolic compounds have been classified as high priority pollutants by EPA (Environmental Protection Agency) of USA. The Ministry of Environment and forest (MOEF), Government of India and EPA of USA have listed phenols on the priority pollutants list. Chronic toxic effects due to phenols reported in humans including vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, fainting and other mental disturbances and excretion of dark urine .[2-3]scientists for the conversion of fly ash into beneficial products while probing doable avenues for allure tenable utilization. Wastewater remediation utilizing Fly ash is one aforementioned attempt solving two together waste administration and water quality issues. Phenols are generated from industrial sources, such as refineries, petrochemical, pharmaceuticals and plastic resin production. Phenols are not only toxic but also carcinogenic in nature[4-5].Phenols have high stability in the aqueous phase and thus causes serious risk to the aqueous environment. Also it is detrimental to human health due to rapid absorption through the skin.[6-8] Phenols have attached much public attention due to its presence in ground water, river and drinking waters. Even in low concentration, Phenols causes toxicity and foul odor to the water.

This is due to its reactivity with chlorine (-Cl) and nitro (-No $_2$) group present in the soil to from chlorophenol and nitro phenol respectively.[9] Most countries specify maximum allowable concentration of phenol in wastewater to be less than 1ppb.[10] The exposure of phenol and its derivative compounds to human and animal causes liver and kidney damage, central nervous system impairment, diarrhea and excretion dark urging.[11-12] This makes it necessary to develop methods that allow one to detect quantity and remove phenol from wastewater. [13]Several conventional methods are available for treating phenolic wastewater which include reverse osmosis, anaerobic processes, the electro Fenton method, combined application of flotation and conjugation process, stripping and oxidation, solver extraction etc.[14] Each of these methods has some disadvantages in their application. Among various methods used in phenol wastewater treatment, 'adsorption'

process is considered better due to its simplicity of design, ease of operation and convenience. Adsorption is a process in which a substance (adsorbate), in gas or liquid phase, accumulates on a solid surface (adsorbent). It is based on the capability of porous materials with large surfaces to selectively retain compounds on the surface of the solid (adsorbent). The extent of adsorption also depends on the nature of the solid surface (adsorbent) especially its porosity and surface area. As such various adsorbents that have high porosity and large surface area thereby facilitating adsorption. Thus, for a good adsorbent, it must have large surface area and requires less time for adsorption equilibrium.[15]Recently, many researchers have been using natural material and industrial by-products including detonate, fly ash and biomass for the removal of inorganic and organic contaminants.

Activated carbon is ,however, an expensive material, so many of the other alternatives suggested become very attractive option, because It is waste product obtained from pruning of coal, it is cheap widely available and has good mechanical stability for handing purposes and employment in adsorption columns. The most important characteristics of flyash are calcium content that provides alkalinity in the system raising plot strongly alkaline value and the Sio_2, Al_20_3 , Fe_20_3 etc content.[16] Research efforts on flyash to date have been focused on the study of mechanism involved in contaminant uptake. A lot of research works have been carried out on the removal of toxic phenols from aqueous solution by activated charcoal and other adsorbents. But work on the removal characteristics of m-chlorophenol by flyash is very scanty. The aim of this present study is to investigate the use of flyash as a low cost adsorbent for the removal of toxic m- chlorophenol from aqueous solutions. The kinetics and mechanism of m- chlorophenol uptake by the flyash is investigated.

MATERIAL AND METHODS

Standard solution of MCP are prepared (500 mg/L) by weighing the purified grade chemical and dissolving them in minimum volume of acetone. Portion of this solution is diluted with distilled water similar to those of real waste-water sample. All reagents are of A.R.grade. Experimental solutions of desired concentration are prepared by successive dilution. FA was obtained from Thermal Power Station Chachai, Anooppur, Shahdol (M.P.) India. The FA is sieved through standard test sieves having size 150, 106, 45μm respectively. The different fraction of FA dried for 2 hours at 110^0C in an electric oven and stored in desiccators for use. The chemical constituents of FA are determined by Indian Standard methods[17] along with other characteristics such as loss on ignition (LOI)at 800^0C,the specific gravity, surface area and porosity and are reported elsewhere [17]shown in Table-1.The chemical compositions of different fractions of FA are also determined by Indian Standard methods[16] and are reported elsewhere [18] as shown in Table-2. The chemical analysis of data indicates that the sample consists of mullite. ($Al_6Si_2O_{13}$), quartz (SiO_2), magnetite (Fe_3O_4), anhydrite ($CaSO_4$), hematite (Fe_2O_3), lime (CaO) as the major phase. The results of other physicochemical methods of analysis such as FTIR, XRD, XRF and SEM-EDS used to determine the mineralogical composition are reported earlier[19]. These fractions of FA are used in batch kinetic experiment without any pretreatment. Batch kinetics adsorption experiment is conducted by shaking 25ml of MCP solution with 1g of FA fraction in100 ml Conical glass Stoppard flask (to avoid Vaporization losses of MCP at various particle sizes (150, 106 and 45µm), pH (2.0, 4.0, 6.5,8.0 and 10.0), concentration of PCP (250, 350 and 500mg/L) and temperature(30, 40 and 50 ^{0}C) using thermostatic shaker at 200 rpm(similar to environmental condition) .The sample are covered during the entire experiment to avoid MCP degradation by photolysis.

The pH of solution is adjusted with HNO_3 or NaOH by using pH-meter. The progress of adsorption is determined by centrifuging the adsorbate-adsorbent solution at predicated intervals of time and analyzed the supernatant liquid using UV-1800 Shimadzu UV- Spectrophotometer by monitoring the absorbance changes at a maximum wavelength of 280 nm. It should be noticed that below 250 nm the absorption band is not specific to Phenolic compound because a lot of organic compounds have an absorption in their spectral windows. Each experiment is performed at least under identical conditions.

RESULTS AND DISCURSSION KINETIC MODELS

In order to investigate the kinetics of adsorption of MCP on FA, the constants of adsorption are determined in terms of the pseudo-first order models. The pseudo-first order equation was first represented by Lagergren:

$\text{Log } (q_e\text{-}q_t) = \log q_e - k\, t/2.303$---------- (1)

Where q_t (mg g^{-1}) is the amount of phenol adsorbed at time t, q_e (mg g^{-1}) is the amount adsorbed at equilibrium and k is equilibrium rate constant of adsorption. The corresponding linear plots of $\log(q_e-q_t)$ versus t depicted in **Fig. 2, 4, 6** and **8** for adsorption of MCP on FA under different conditions indicate the validity of applying equation (1) to the system known as Lagergren equation and relates to a pseudo first -order sorption process. The value of rate constant, k, for adsorption of MCP on FA under different condition is calculated from the slopes of these plots and is given in **Table 3**.

EFFECT OF PARTICLE SIZE

The effect of particle size for kinetics of MCP on FA is studied. The experimental kinetic curves are presented in **Fig 1**.The experimental data are described by pseudo-first-order model and are given in **Table 3**. The correlations between the particle size and the values of adsorption rate are inversely proportional i.e. the decrease in particle size from 150μm to 45μm caused increase k (rate constant) values i.e. k (150 μm) < k (106 μm) < k (45 μm) as calculated from linear plots of **Fig. 2**.The silica and alumina contents of fly ash play a major role in the sorption of MCP. The reason for this trend may be attributed to the fact that there is strong chemical bonding between lone pair of electron present on the -OH group in the phenol and the central ion of silicate (Si+4) as well as the weakly acidic alumina surface of FA. The higher removal rate of chloro-substituted phenol is due to the introduction of a chloro group (-Cl) into the benzene ring which increase the acid character (conjugation effect) responsible for forming an anion on the oxygen atom of the –OH group and which has a strong affinity for alumina and silica surfaces. It is also obvious that in MCP both functional groups may be separately or simultaneously involved in the adsorption process. [16] The surface area also increased as the particle size decreased. Hence, in addition to the increase in alumina and silica content with decreasing particle size, the increase in the specific surface area also contributed to the observed enhanced adsorption of MCP onto the flash fraction containing the smallest particles .A similar observations are also reported in the study on the adsorption of 3-chlorophenol (MCP) on activated carbon[19]as well as sorption dynamic for removal of phenol from water and waste-water onto bituminous coal. [20]

EFFECT OF pH

The experimental kinetic curves are presented in **Fig 3**. The pH values used in this study are 2.0, 4.0, 6.5, 8.0, and 10.0 for the sorption of phenol on FA. The experimental results are described by the pseudo-first order rate constant, k, of adsorption at various pH values (determined from the linear plots of **Fig. 4**) and are listed in Table 3. This Table shows that there is a decrease in the sorption rate with increase in pH of the solution. The chemical process of MCP in aqueous solution in presence of FA can be represented as

$$H2O + M^{+} \overset{H^{+}}{\leftarrow} MOH \overset{OH^{-}}{\rightarrow} MO^{-} + H2O$$

At lower pH ,the lone pair of electrons on oxygen atom of un-dissociated-OH group present in benzene ring co-ordinates with highly positively charged surface .But at higher pH , the dissociated phenoxide ion (C6H5O–) is expelled by highly negatively charged oxide surface. [21]

Thus the rate constant, k at different pH values are as follows: k (pH 2.0)>k (pH 4.0)>k(pH 6.5)> k(pH 8.0)>k(pH 10.0) The trend is similar to the sorption of nitro -substituted phenols on flyash [22] as well as sorption dynamic for removal of phenol from water and waste-water onto bituminous coal[19].

EFFECT OF CONCENTRATION

The effect of concentration on kinetics of MCP on FA is investigated. **Fig. 5** presents the experimental kinetics curve with MCP concentration in the range 250-500 mg/L. Obviously the increase in concentration of the solution leads to a decrease in the sorption rate constant. From the plot **(Fig. 5)** it could be seen that equilibrium is established after 120 minutes from the beginning of the process. The experimental results are described by the pseudo-first-order model of Lagergren **(Fig. 6)** and from this the rate constants are calculated. As shown in **Table 3** the values of rate constant decreased with an increase in initial MCP concentration which can be shown as k (500 mg L^{-1}) < k (350 mg L^{-1}) < k (250 mg L^{-1})

This is due to the fact that at higher concentration the fractional adsorption is low. [23] Similar observations are reported in the study of Equilibrium, Kinetic and Thermodynamic Studies on Phenol Sorption to Clay [24] as well as sorption dynamic for removal of phenol from water and waste-water onto bituminous coal[20]

EFFECT OF TEMPERATURE

The sorption experiments are conducted at various temperatures in the range 30°C to 50°C with FA **(Fig.7)** which shows that adsorption rate constant increases with increasing in temperature shown in **Table 3(**calculated from **Fig.8)** as

$$k\ (50^{o}C) > k\ (40^{o}C) > k\ (30^{o}C)$$

Indicating the process to be the endothermic. The results suggest that the active surface centers available for the sorption are increased with temperature[25]. Similar observation is also reported in the study for sorption of phenol and m-nitro phenol on clay[26-27] **a**s well as sorption dynamic for removal of phenol from water and waste-water onto bituminous coal.

CONCLUSION

The present study shows the potential of FA as adsorbent for phenolic wastewater treatment .This treatment is simple and economic. Such a batch system will be applicable to small industries generating phenols containing wastewaters. The sorption kinetics data thus generated may be used for designing a treatment plant for phenolic effluents wherein continuous removal or collection can be achieved on a large scale.

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Table -1 Characteristics of flyash

Element as oxide	Weight %
SiO_2	59.54
Al_2O_3	27.20
Fe_2O_3	4.87
CaO	2.91
MgO	0.40
K_2O+Na_2O	1.00
LOI (800^0 C)	12.00
Specific gravity	1.80
Surface Area	7000 – 9000 cm^2
Porosity	0.34 - 0.62

Table – 2 chemical analysis of Fraction of Flyash Chemical Composition (Percentage by weight)

Particle Size μm	**SiO_2**	**AI_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**LOI 800^0C**
150 μm	59.54	27.20	4.87	2.91	0.40	12
106μm	67.00	30.00	6.10	3.80	1.10	08
45 μm	77.75	36.00	6.00	4.00	1.50	4.09

Table -3 Pseudo- first- order (Lagergren) rate constant of MCP on flyash

Sorbate Rate	**Condition**		**Rate constant(min^{-1})**	**R^2**
	Particle Size (μm)	150	4.83 x 10^{-2}	0.994
		106	5.07 x 10^{-2}	0.990
		45	5.56 x 10^{-2}	0.993

meta - chlorophenol (MCP)	pH	2.0	5.76×10^{-2}	0.992
		4.0	5.29×10^{-2}	0.993
		6.5	4.84×10^{-2}	0.994
		8.0	4.38×10^{-2}	0.993
		10.0	3.92×10^{-2}	0.986
	Concentration (mg/L)	250	4.84×10^{-2}	0.991
		350	5.06×10^{-2}	0.993
		500	5.53×10^{-2}	0.994
	Temperature (K)	303	4.84×10^{-2}	0.994
		313	5.07×10^{-2}	0.994
		323	5.30×10^{-2}	0.992

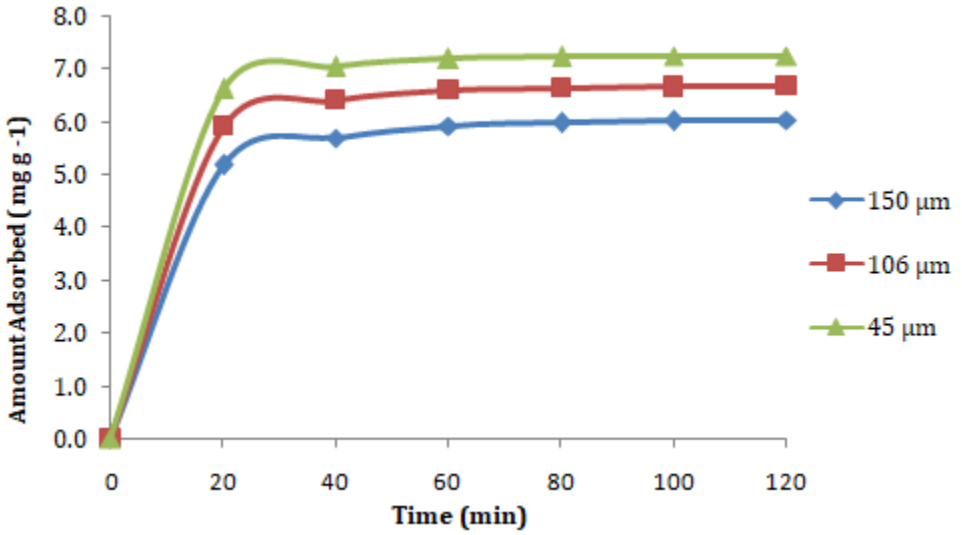


Fig.1 Adsorption Kinetics of m- chlorophenol on flyash; condition : 500 mgl $^{-1}$; pH 6.5 ; Temperature 30°C

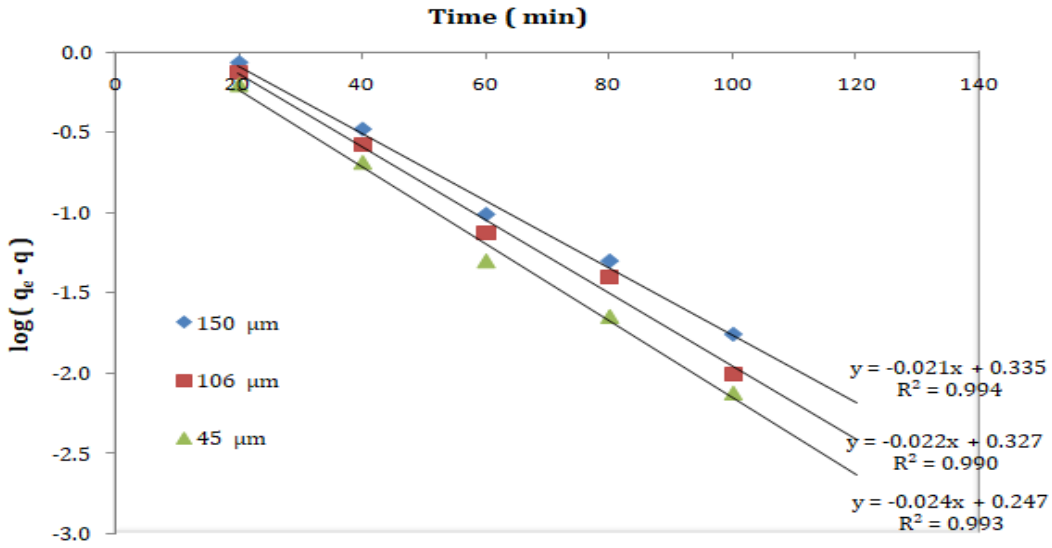
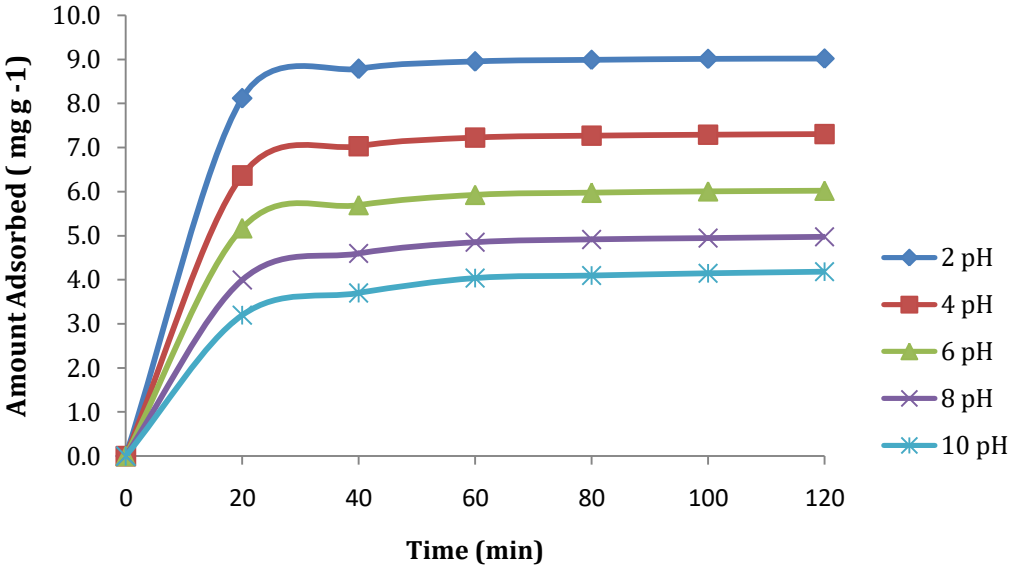


Fig. 2 Lagergren plot for the adsorption of m - chlorophenol on flyash;Concentration 500 mgl^{-1}; pH 6.5; Temerature 30°C



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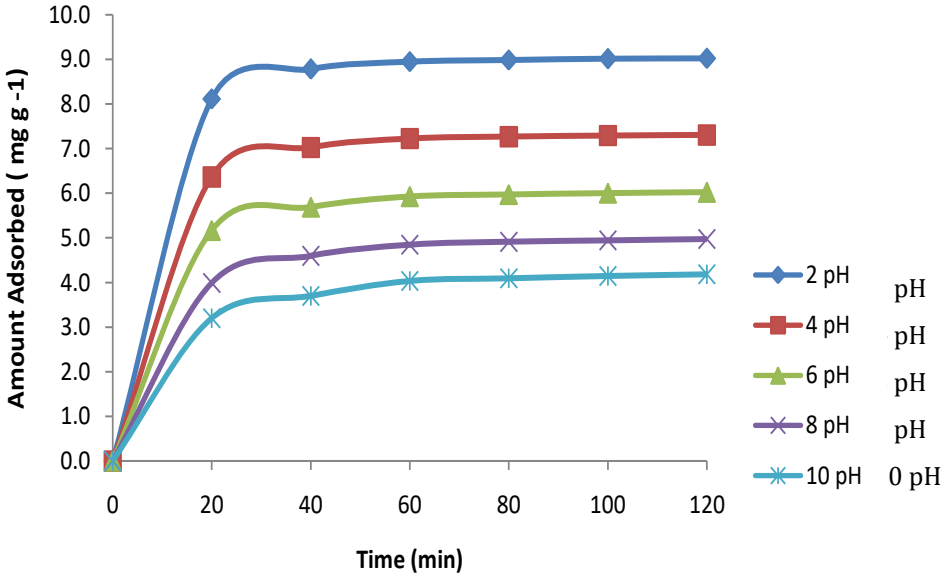

Fig.3 Adsorption Kinetics of m- chlorophenol on flyash; condition : 500 mgl $^{-1}$; size 150 µm; Temperature 30°C

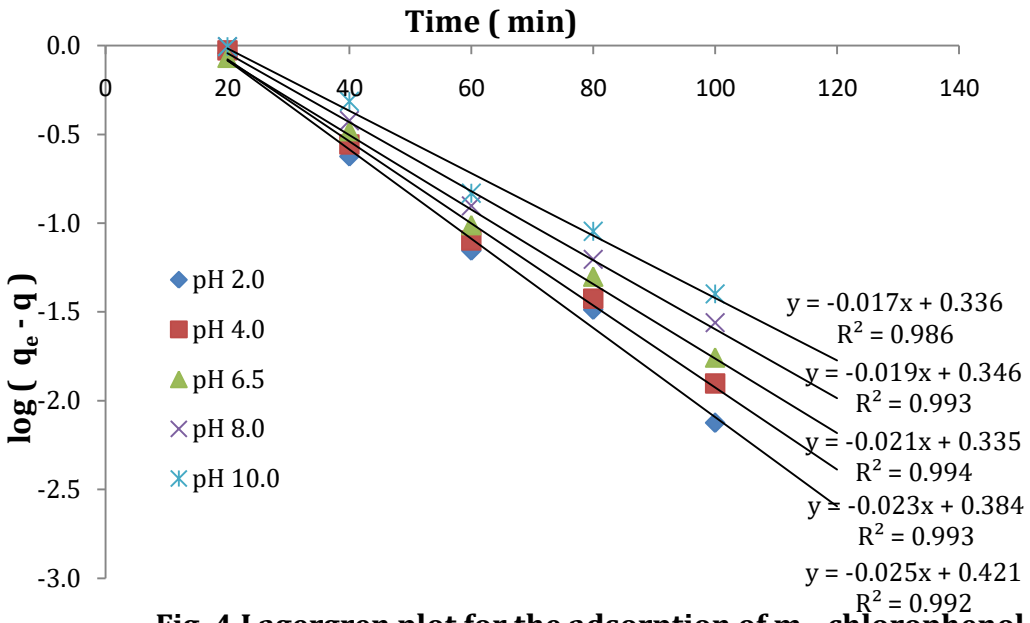

Fig. 4 Lagergren plot for the adsorption of m - chlorophenol on flyash;Concentration 500 mgl^{-1}; Size 150µm ; Temerature 30°C

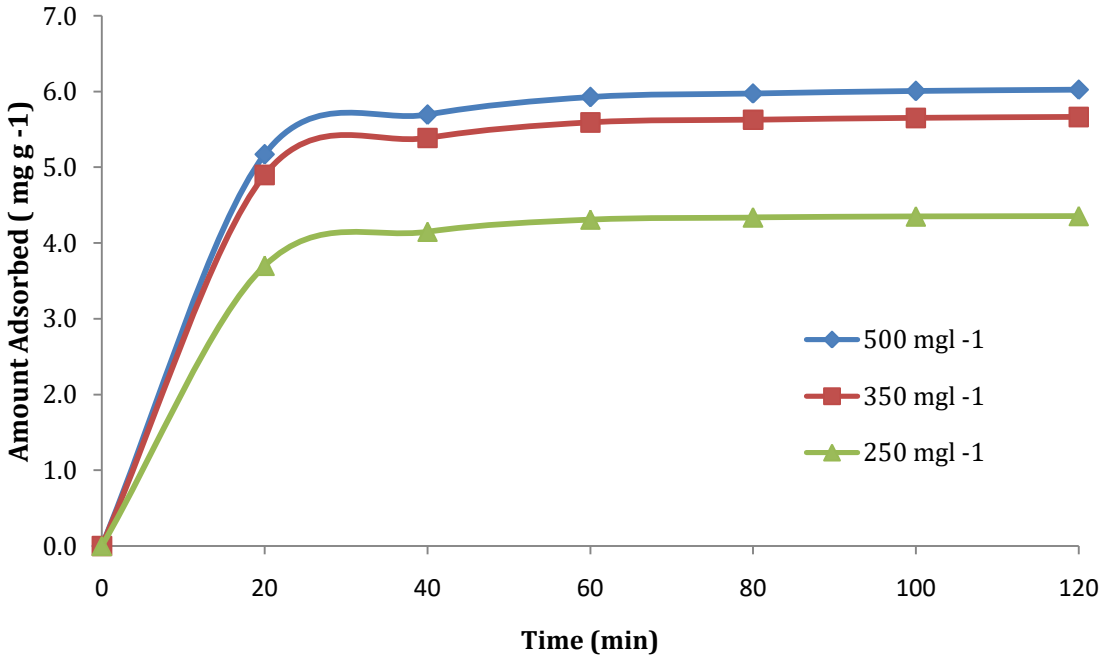

Fig.5 Adsorption Kinetics of m- chlorophenol on flyash; condition : pH 6.5 ; size 150 µm; Temperature 30°C

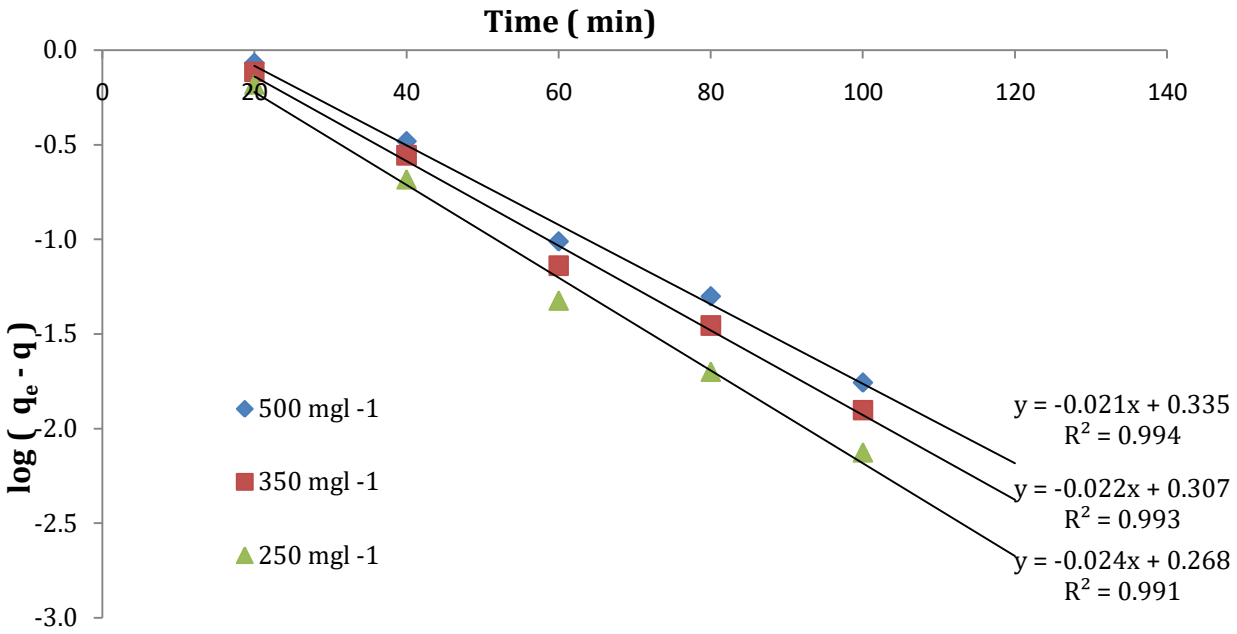

Fig. 6 Lagergren plot for the adsorption of m - chlorophenol on flyash;Particle size 150 µm ; pH 6.5; Temerature 30°C

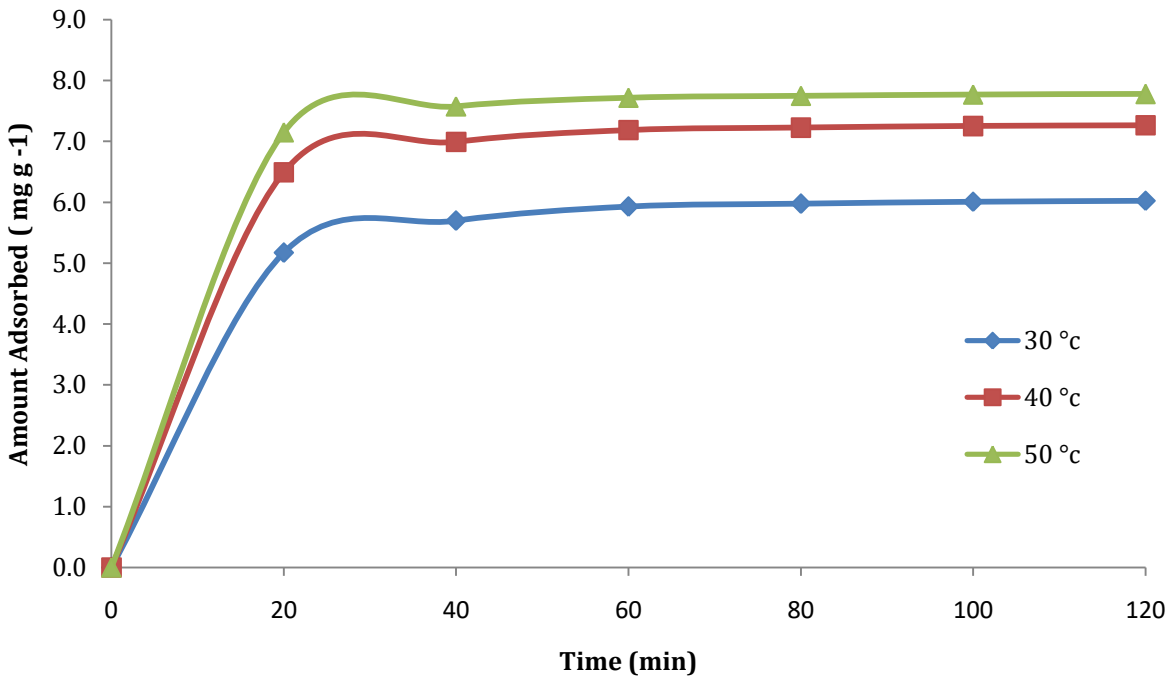

Fig.7 Adsorption Kinetics of m- chlorophenol on flyash; condition : 500 mgl $^{-1}$; pH 6.5 ; size 150 µm

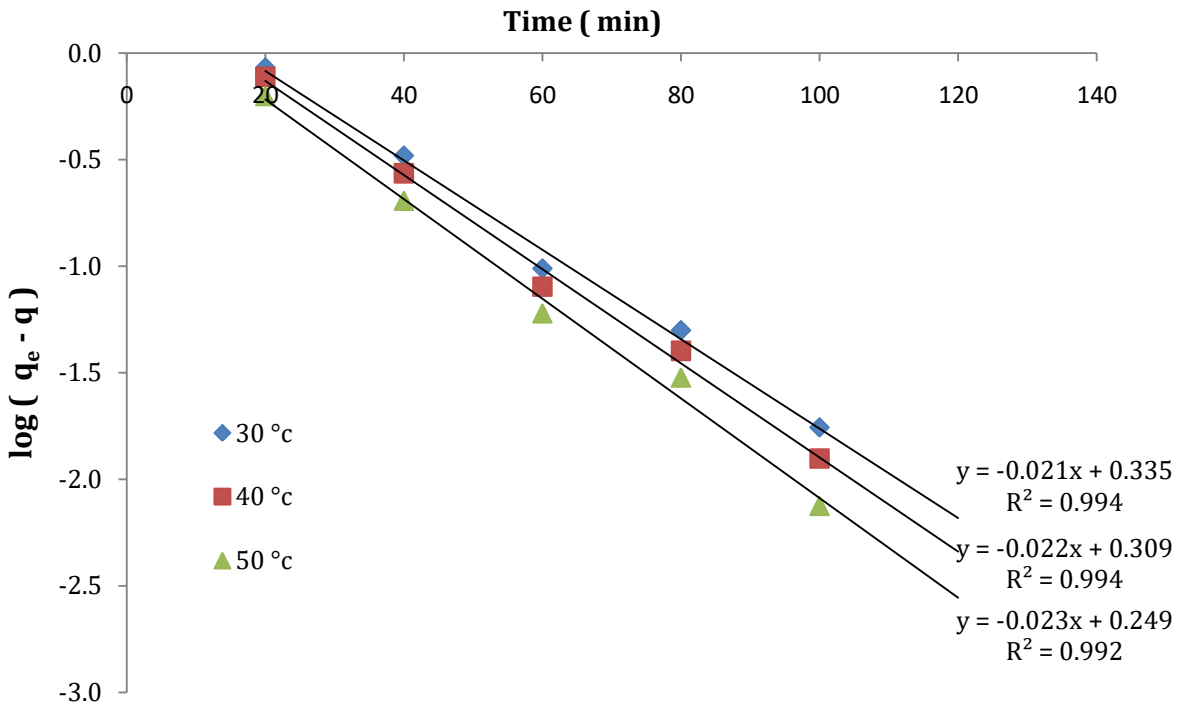

Fig. 8 Lagergren plot for the adsorption of m - chlorophenol on flyash;Concentration 500 mgl^{-1}; Size 150µm ; pH 6.5 .